

made with the method, and the correction procedure shall become a part of the method.

EFFECTIVE DATE NOTE: At 75 FR 35601, June 22, 2010, § 53.32 was amended by revising paragraph (e)(2), effective Aug. 23, 2010. For the convenience of the user, the revised text is set forth as follows:

**§ 53.32 Test procedures for methods for SO<sub>2</sub>, CO, O<sub>3</sub>, and NO<sub>2</sub>.**

\* \* \* \* \*

(e) \* \* \*

(2) For a candidate method having more than one selectable range, one range must be that specified in table B-1 of subpart B of this part, and a test analyzer representative of the method must pass the tests required by this subpart while operated on that range. The tests may be repeated for one or more broader ranges (*i.e.*, ones extending to higher concentrations) than the one specified in table B-1 of subpart B of this part, provided that such a range does not extend to concentrations more than four times the upper range limit specified in table B-1 of subpart B of this part and that the test analyzer has passed the tests required by subpart B of this part (if applicable) for the broader range. If the tests required by this subpart are conducted or passed only for the range specified in table B-1 of subpart B of this part, any equivalent method determination with respect to the method will be limited to that range. If the tests are passed for both the specified range and a broader range (or ranges), any such determination will include the broader range(s) as well as the specified range. Appropriate test data shall be submitted for each range sought to be included in such a determination.

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**§ 53.33 Test Procedure for Methods for Lead (Pb).**

(a) *General.* The reference method for Pb in TSP includes two parts, the reference method for high-volume sampling of TSP as specified in 40 CFR 50, appendix B and the analysis method for Pb in TSP as specified in 40 CFR 50, appendix G. Correspondingly, the reference method for Pb in PM<sub>10</sub> includes the reference method for low-volume sampling of PM<sub>10</sub> in 40 CFR 50, appendix O and the analysis method of Pb in PM<sub>10</sub> as specified in 40 CFR 50, appendix Q. This section explains the procedures for demonstrating the equivalence of either a candidate method for

Pb in TSP to the high-volume reference methods, or a candidate method for Pb in PM<sub>10</sub> to the low-volume reference methods.

(1) Pb in TSP—A candidate method for Pb in TSP specifies reporting of Pb concentrations in terms of standard temperature and pressure. Comparisons of candidate methods to the reference method in 40 CFR 50, appendix G must be made in a consistent manner with regard to temperature and pressure.

(2) Pb in PM<sub>10</sub>—A candidate method for Pb in PM<sub>10</sub> must specify reporting of Pb concentrations in terms of local conditions of temperature and pressure, which will be compared to similarly reported concentrations from the reference method in 40 CFR 50 appendix Q.

(b) *Comparability.* Comparability is shown for Pb methods when the differences between:

(1) Measurements made by a candidate method, and

(2) Measurements made by the reference method on simultaneously collected Pb samples (or the same sample, if applicable), are less than or equal to the values specified in table C-3 of this subpart.

(c) *Test measurements.* Test measurements may be made at any number of test sites. Augmentation of pollutant concentrations is not permitted, hence an appropriate test site or sites must be selected to provide Pb concentrations in the specified range.

(d) *Collocated samplers.* The ambient air intake points of all the candidate and reference method collocated samplers shall be positioned at the same height above the ground level, and between 2 meters (1 meter for samplers with flow rates less than 200 liters per minute (L/min)) and 4 meters apart. The samplers shall be oriented in a manner that will minimize spatial and wind directional effects on sample collection.

(e) *Sample collection.* Collect simultaneous 24-hour samples of Pb at the test site or sites with both the reference and candidate methods until at least 10 sample pairs have been obtained.

(1) A candidate method for Pb in TSP which employs a sampler and sample collection procedure that are identical to the sampler and sample collection

procedure specified in the reference method in 40 CFR part 50, Appendix B, but uses a different analytical procedure than specified in 40 CFR Appendix G, may be tested by analyzing pairs of filter strips taken from a single TSP reference sampler operated according to the procedures specified by that reference method.

(2) A candidate method for Pb in  $PM_{10}$  which employs a sampler and sample collection procedure that are identical to the sampler and sample collection procedure specified in the reference method in 40 CFR part 50, Appendix O, but uses a different analytical procedure than specified in 40 CFR Appendix Q, requires the use of two  $PM_{10}$  reference samplers because a single 46.2-mm filter from a reference sampler may not be divided prior to analysis. It is possible to analyze a 46.2-mm filter first with the non-destructive X-ray Fluorescence (XRF) FRM and subsequently extract the filter for other analytical techniques. If the filter is subject to XRF with subsequent extraction for other analyses, then a single  $PM_{10}$  reference sampler may be used for sample collection.

(3) A candidate method for Pb in TSP or Pb in  $PM_{10}$  which employs a direct reading (e.g., continuous or semi-continuous sampling) method that uses the same sampling inlet and flow rate as the FRM and the same or different analytical procedure may be tested. The direct measurements are then aggregated to 24-hour equivalent concentrations for comparison with the FRM. For determining precision in section (k), two collocated direct reading devices must be used.

(f) *Audit samples.* Three audit samples must be obtained from the address given in § 53.4(a). For Pb in TSP collected by the high-volume sampling method, the audit samples are  $\frac{3}{4}$  x 8-inch glass fiber strips containing known amounts of Pb in micrograms per strip ( $\mu\text{g}/\text{strip}$ ) equivalent to the following nominal percentages of the National Ambient Air Quality Standard (NAAQS): 30%, 100%, and 250%. For Pb in  $PM_{10}$  collected by the low-volume sampling method, the audit samples are 46.2-mm polytetrafluorethylene (PTFE) filters containing known amounts of Pb in micrograms per filter

( $\mu\text{g}/\text{filter}$ ) equivalent to the same percentages of the NAAQS: 30%, 100%, and 250%. The true amount of Pb (Tqi), in total  $\mu\text{g}/\text{strip}$  (for TSP) or total  $\mu\text{g}/\text{filter}$  (for  $PM_{10}$ ), will be provided for each audit sample.

(g) *Filter analysis.*

(1) For both the reference method samples (e) and the audit samples (f), analyze each filter or filter extract three times in accordance with the reference method analytical procedure. This applies to both the Pb in TSP and Pb in  $PM_{10}$  methods. The analysis of replicates should not be performed sequentially, i.e., a single sample should not be analyzed three times in sequence. Calculate the indicated Pb concentrations for the reference method samples in micrograms per cubic meter ( $\mu\text{g}/\text{m}^3$ ) for each analysis of each filter. Calculate the indicated total Pb amount for the audit samples in  $\mu\text{g}/\text{strip}$  for each analysis of each strip or  $\mu\text{g}/\text{filter}$  for each analysis of each audit filter. Label these test results as  $R_{1A}$ ,  $R_{1B}$ ,  $R_{1C}$ ,  $R_{2A}$ ,  $R_{2B}$ , etc.,  $Q_{1A}$ ,  $Q_{1B}$ ,  $Q_{1C}$ , etc., where R denotes results from the reference method samples; Q denotes results from the audit samples; 1, 2, 3 indicate the filter number, and A, B, C indicate the first, second, and third analysis of each filter, respectively.

(2) For the candidate method samples, analyze each sample filter or filter extract three times and calculate, in accordance with the candidate method, the indicated Pb concentration in  $\mu\text{g}/\text{m}^3$  for each analysis of each filter. The analysis of replicates should not be performed sequentially. Label these test results as  $C_{1A}$ ,  $C_{1B}$ ,  $C_{2C}$ , etc., where C denotes results from the candidate method. For candidate methods which provide a direct reading or measurement of Pb concentrations without a separable procedure,  $C_{1A}=C_{1B}=C_{1C}$ ,  $C_{2A}=C_{2B}=C_{2C}$ , etc.

(h) *Average Pb concentration.* For the reference method, calculate the average Pb concentration for each filter by averaging the concentrations calculated from the three analyses as described in (g)(1) using equation 1 of this section:

## Equation 1

$$R_{iave} = \frac{(R_{iA} + R_{iB} + R_{iC})}{3}$$

Where, i is the filter number.

(i) *Analytical Bias.* (1) For the audit samples, calculate the average Pb concentration for each strip or filter analyzed by the reference method by averaging the concentrations calculated from the three analyses as described in (g)(1) using equation 2 of this section:

## Equation 2

$$Q_{iave} = \frac{(Q_{iA} + Q_{iB} + Q_{iC})}{3}$$

Where, i is audit sample number.

(2) Calculate the percent difference ( $D_{qi}$ ) between the average Pb concentration for each audit sample and the true Pb concentration ( $T_{qi}$ ) using equation 3 of this section:

## Equation 3

$$D_{qi} = \frac{Q_{iave} - T_{qi}}{T_{qi}} \times 100$$

(3) If any difference value ( $D_{qi}$ ) exceeds  $\pm 5$  percent, the bias of the reference method analytical procedure is out-of-control. Corrective action must be taken to determine the source of the error(s) (e.g., calibration standard discrepancies, extraction problems, etc.) and the reference method and audit sample determinations must be repeated according to paragraph (g) of this section, or the entire test procedure (starting with paragraph (e) of this section) must be repeated.

(j) *Acceptable filter pairs.* Disregard all filter pairs for which the Pb concentration, as determined in paragraph (h) of this section by the average of the three reference method determinations, falls outside the range of 30% to 250% of the Pb NAAQS level in  $\mu\text{g}/\text{m}^3$  for Pb in both TSP and  $\text{PM}_{10}$ . All remaining filter pairs must be subjected to the tests for precision and comparability in paragraphs (k) and (l) of this section. At least five filter pairs must be within the specified concentration range for the tests to be valid.

(k) *Test for precision.* (1) Calculate the precision (P) of the analysis (in percent) for each filter and for each method, as the maximum minus the minimum divided by the average of the three concentration values, using equation 4 or equation 5 of this section:

## Equation 4

$$P_{Ri} = \frac{R_{i\max} - R_{i\min}}{R_{iave}} \times 100$$

or

## Equation 5

$$P_{Ci} = \frac{C_{i\max} - C_{i\min}}{C_{iave}} \times 100$$

Where, i indicates the filter number.

(2) If a direct reading candidate method is tested, the precision is determined from collocated devices using equation 5 above.

(3) If any reference method precision value ( $P_{Ri}$ ) exceeds 15 percent, the precision of the reference method analytical procedure is out-of-control. Corrective action must be taken to determine the source(s) of imprecision, and the reference method determinations must be repeated according to paragraph (g) of this section, or the entire test procedure (starting with paragraph (e) of this section) must be repeated.

(4) If any candidate method precision value ( $P_{Ci}$ ) exceeds 15 percent, the candidate method fails the precision test.

(5) The candidate method passes this test if all precision values (i.e., all  $P_{Ri}$ 's and all  $P_{Ci}$ 's) are less than 15 percent.

(l) *Test for comparability.* (1) For each filter or analytical sample pair, calculate all nine possible percent differences (D) between the reference and candidate methods, using all nine possible combinations of the three determinations (A, B, and C) for each method using equation 6 of this section:

## Equation 6

$$D_{in} = \frac{C_{ij} - R_{jk}}{R_{jk}} \times 100$$

Where, i is the filter number, and n numbers from 1 to 9 for the nine possible difference

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combinations for the three determinations for each method (j = A, B, C, candidate; k = A, B, C, reference).

(2) If none of the percent differences (D) exceeds  $\pm 20$  percent, the candidate method passes the test for comparability.

(3) If one or more of the percent differences (D) exceed  $\pm 20$  percent, the candidate method fails the test for comparability.

(4) The candidate method must pass both the precision test (paragraph (k) of this section) and the comparability test (paragraph (1) of this section) to qualify for designation as an equivalent method.

(m) *Method Detection Limit (MDL)*. Calculate the estimated MDL using the guidance provided in 40 CFR, Part 136 Appendix B. It is essential that all sample processing steps of the analytical method be included in the determination of the method detection limit. Take a minimum of seven blank filters from each lot to be used and calculate the detection limit by processing each through the entire candidate analytical method. Make all computations according to the defined method with the final results in  $\mu\text{g}/\text{m}^3$ . The MDL of the candidate method must be equal to, or less than 5% of the level of the Pb NAAQS.

[73 FR 67057, Nov. 12, 2008]

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\* \* \* \* \*

(e) \* \* \*

(2) For a candidate method having more than one selectable range, one range must be that specified in table B-1 of subpart B of this part, and a test analyzer representative of the method must pass the tests required by this subpart while operated on that range. The tests may be repeated for one or more broader ranges (*i.e.*, ones extending to higher concentrations) than the one specified in table B-1 of subpart B of this part, provided that such a range does not extend to concentrations more than four times the upper range limit specified in table B-1 of subpart B of this part and that the test analyzer has passed the tests required by subpart B of this

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part (if applicable) for the broader range. If the tests required by this subpart are conducted or passed only for the range specified in table B-1 of subpart B of this part, any equivalent method determination with respect to the method will be limited to that range. If the tests are passed for both the specified range and a broader range (or ranges), any such determination will include the broader range(s) as well as the specified range. Appropriate test data shall be submitted for each range sought to be included in such a determination.

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### § 53.34 Test procedure for methods for PM<sub>10</sub> and Class I methods for PM<sub>2.5</sub>.

(a) *Comparability*. Comparability is shown for PM<sub>10</sub> methods and for Class I methods for PM<sub>2.5</sub> when the relationship between:

(1) Measurements made by a candidate method, and

(2) Measurements made by a corresponding reference method on simultaneously collected samples (or the same sample, if applicable) at each of one or more test sites (as required) is such that the linear regression parameters (slope, intercept, and correlation coefficient) describing the relationship meet the requirements specified in table C-4 of this subpart.

(b) *Methods for PM<sub>10</sub>*. Test measurements must be made, or derived from particulate samples collected, at not less than two test sites, each of which must be located in a geographical area characterized by ambient particulate matter that is significantly different in nature and composition from that at the other test site(s). Augmentation of pollutant concentrations is not permitted, hence appropriate test sites must be selected to provide the minimum number of test PM<sub>10</sub> concentrations in the ranges specified in table C-4 of this subpart. The tests at the two sites may be conducted in different calendar seasons, if appropriate, to provide PM<sub>10</sub> concentrations in the specified ranges.

(c) *PM<sub>10</sub> methods employing the same sampling procedure as the reference method but a different analytical method*. Candidate methods for PM<sub>10</sub> which employ a sampler and sample collection procedure that are identical to the sampler